RAW MATERIALS

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DIATOMITES OF KARELIA FOR GLASS PRODUCTION

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Two specimens of lake diatomites of Karelia differing by the rock-forming types of diatoms and the form, size, and degree of preservation of the valves are investigated. It is determined that the size of the valves has a large effect on the granulometric composition and physical-chemical properties of diatomites. The SiO_2 content in the initial samples of diatomites is 70%. After heat-treatment and leaching it increases to 91% and the iron content decreases sharply to 0.075%. After impurities have been removed, lake diatomites are of interest for the production of sheet glass, crystal articles, glazes and enamels, silicate glasses, as well as ceramic articles.

The diatomites of Karelia are silica-bearing amorphous sedimentary rock. In their natural state these diatomites (moisture content 80 – 85%) comprise a brown and less often white, cream, or orange colors gelatinous (gel) mass, more than 50%[2] of which consists of siliceous (opaline) valves of microscopic algae — diatoms [1].

There are 128 known deposits and manifestations of diatomites on the territory of Karelia. The diatomites of Karelia lie on the bottom of small lakes and swamps. The thickness of the deposits averages 2 – 3 m, reaching 6 – 8 m in some water reservoirs.

The most promising regions of Karelia where deposits and manifestations of diatomites have been found are Muezerskii and Loukhskii rayons. The deposits found here are located close to roads and train tracks, which makes it possible working these deposits effectively and to transport the raw materials obtained. Samples of diatomites from these regions were obtained for investigation.

The content of SiO_2 in the natural samples of diatomites reaches 50 – 90%. The admixture of sesquioxides is small on the whole, but it fluctuates over wide limits (Al_2O_3 — 0.5 – 6.5%, Fe_2O_3 — 0 – 7%) and depends on the degree of contamination of the diatomites by mineral particles. The content of organic impurities also varies over a wide range — from 0 to 34%.

On account of the variability of the composition of diatomites, two samples were investigated. The samples differed by their content of silica, mineral impurities, organic inclusions, and valve sizes. Sample D-00-50 was obtained from Lake Tedrilampi (Muezerskii rayon); this sample is brown. Sample D-01-23 was obtained from a nameless endorheic lake located 2 km from Tungozero (Loukhskii rayon); this sample is white. The chemical compositions are presented in Table 1, and the physical-chemical properties of the diatomites after calcination and leaching are presented in Table 2.

The mineral composition of the samples was determined by optical microscopy, x-ray phase analysis, and DTA. Granulometric analysis was performed in a LS 13320 laser particle analyzer in the particle size range from 0.01 to 2000 μm. The specific surface area was determined by chromatography using a GKh-1 gas (nitrogen) analyzer.

A particularity of lake diatomites is the diversity of the rock-forming types, distinguished by form, dimensions, and degree of preservation of the valves. The content of whole valves can serve as a quality indicator of the diatomites [2]. It has been established that the rock-forming types of sample D-01-23 are bottom pennate and plankton centric, cylindrical types with valves of different sizes ranging from 30 – 40 to 100 – 150 μm — type IV [1] (Fig. 1*a* and *b*). The D-00-50 sample is represented by diatoms of a different type where fine pennate forms with valves up to 30 μm — type II (Fig. 1*c* and *d*) — are the rock-forming types.

According to optical microscopy the experimental samples of diatoms consist mainly of amorphous silica and organic impurities. Quartz and feldspar grains of size 0.015 –

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[2] Here and below — content by weight.

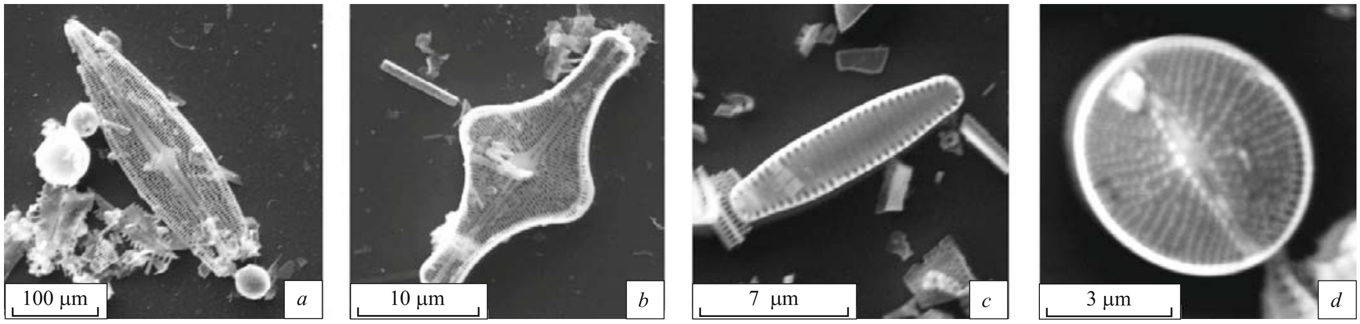

Fig. 1. Rock-forming types of diatomites characteristic for the D-01-23 (*a*, *b*) and D-00-50 (*c*, *d*) samples.

0.030 mm and seldomly 0.2 mm are present as mineral impurities. Rare grains are brown due to iron oxides.

DTA established that up to 1000°C an endothermal effect is observed in the low-temperature range with a maximum at 110°C, corresponding to the removal of adsorption water. A quite strong exothermal effect is observed at 285°C, especially in the D-00-50 sample; this is characteristic for organic matter and oxidation of Fe^{2+} in chlorite. A transition of amorphous silicon into a low-temperature crystalline form (β-quartz) occurs in the temperature range 480 – 580°C.

For the most part, lake diatomites require enrichment, during which organic and mineral impurities are removed. To remove organic substances and mineral impurities the diatomite samples were calcined in a muffle furnace at 700°C for 1.5 h and then underwent magnetic separation and leaching (boiling in 5% HCl for 1 h).

After calcination and subsequent boiling in 5% HCl the iron oxide content in the experimental diatomite sample drops sharply to 0.07% in D-01-23 and 0.09% in D-00-50, and the silicon dioxide content increases by 25 – 30% (see Table 1). The valve size decreases to 15 μm, as electron microscopy of D-10-23 samples shows (Fig. 2*a*). The presence of a structureless disordered state characteristic of amorphous silica is observed in the electron diffraction pattern of this sample (Fig. 2*b*).

An increase of the integral intensity (halo) in the x-ray diffraction patterns indicates the presence of x-ray amorphous matter in the initial diatomite samples. The shift of the integral intensity of the halo in the D-01-23 sample after heat-treatment and leaching as compared with the initial sample is evidently due to the differences of the chemical composition. This is a consequence of an increase of the silica content after leaching (see Table 1).

According to optical microscopy, a distinguishing feature of the two diatomite samples is the different size of the valves. This is confirmed by an investigation, using a laser analyzer, of the sizes of the finely disperse particles of the initial diatomite samples and after their leaching. It was de-

TABLE 1.

Diatomite	Content, wt.%								
	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	calcinated losses
Initial D-01-23:	76.20	0.10	3.82	0.22	0.25	0.28	0.33	0.27	18.53
calcined at 700°C	88.86	0.08	4.32	0.13	0.41	0.37	0.29	0.19	5.35
after boiling in HCl	91.20	0.05	4.43	0.07	0.92	0.43	0.08	0.03	2.79
Initial D-00-50:	70.46	0.05	1.96	2.27	0.62	0.43	0.19	0.14	23.88
calcined at 700°C	86.02	0.06	2.29	2.05	1.38	0.51	0.24	0.18	7.27
after boiling in HCl	88.28	0.05	2.38	0.09	1.62	0.58	0.76	0.33	5.91

TABLE 2.

Diatomite	Mass density, g/cm^3	Specific surface area, m^2/g, after boiling in HCl	Thermal conductivity, W/(m · K)	True density, g/cm^3	Total iron content, %	Other, %	Color after leaching
D-01-23	0.19	123.0	0.07	2.3	0.07	3.22	White
D-00-50	0.45	14.8	0.10	3.4	0.09	8.50	Light yellow

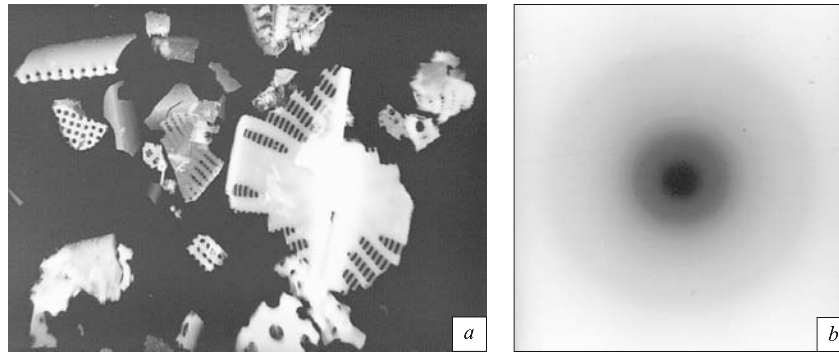

Fig. 2. Sample D-01-23 (× 4000, *a*) and its electron diffraction pattern (*b*): *1*) initial diatomite; *2*) diatomite after leaching.

termined that the valve sizes in the initial D-01-23 sample vary over wide limits (presence of peaks at 15, 45, 150, and 550 μm), of which the 15 μm particles predominate (Fig. 3*a*). After heat-treatment and leaching, the content of the 15 μm fraction in this sample doubles.

The predominant particle sizes in the D-00-50 sample are 150 and 450 μm, as is indicated by the strongest peaks (Fig. 3*b*). Post-leaching the content of large mineral particles (450 μm) is much lower and only 20 – 150 μm diatom valves remain.

The dispersity of the particles was determined more accurately by determining the specific surface area of a diatomite. This area affects the behavior of the powders during the formation of the mixes and during sintering; this is of great importance for obtaining glasses and ceramics. It depends on the particle size and shape. Post-leaching the D-01-23 sample is characterized by a larger specific surface (123 m^2/g) than the D-00-50 sample (14.8 m^2/g). This is a consequence of the greater dispersity and porosity of the D-01-23 (type IV) sample as compared with the D-00-50 (type II) sample.

The different rock-forming type and granulometric composition of the experimental samples of diatomites have a large effect on the volume mass: 0.19 g/cm^3 for D-01-23 and 0.45 g/cm^3 for D-00-50 (see Table 2). The diatomites have a low thermal conductivity — 0.07 – 0.10 W/(m · K). The density of the D-01-23 sample is close to the density of amorphous quartz (2.3 g/cm^3).

The experimental samples of diatomites differ by their physical – chemical properties depending on their water composition and the degree of preservation and number of the valves as well as on the quantity of organic and mineral impurities. They have a finely disperse amorphous structure and are distinguished by a high content of silica and very low content of iron oxide after leaching. All these properties make such diatomites potentially widely useful.

The lake diatomites of Karelia are an interesting but still little-studied siliceous material. According to their chemical composition and physical-mechanical properties (see Tables 1 and 2) the diatomites of Karelia meet the requirements for diatomaceous raw material suitable for manufacturing light-weight heat-insulating brick, as fill in thermal insulation, and filler for heat-resistant concretes used in construction. Our view is that the D-00-50 diatomites are best used as adsorbents and fillers and the D-01-23 diatomites as raw materials for glass production. Diatomites appear to be a promising material for the glass industry and for making glazes and enamels after mineral and organic impurities are removed.

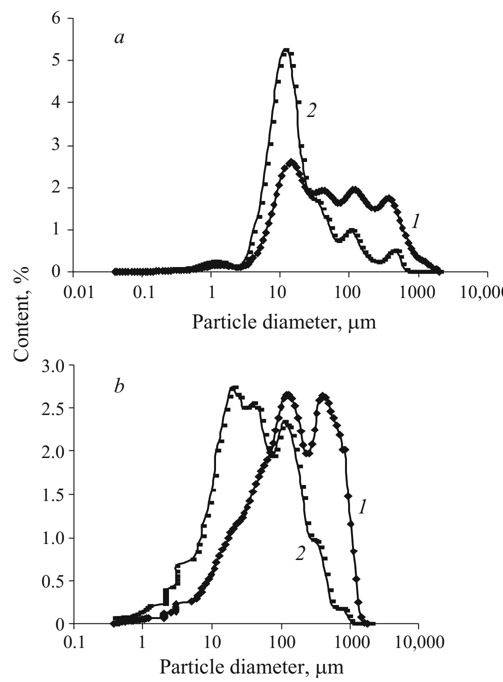

Fig. 3. Content of finely disperse particles in the D-01-23 (*a*) and D-00-50 (*b*) samples: *1*) initial diatomite; *2*) diatomite after leaching.

Silica-containing amorphous rocks used in the production of glass instead of raw materials with a crystalline structure (quartz sand and others) make it possible to intensify the glass formation process as a result of the high reactivity of amorphous silica. Hydrothermal-alkali treatment of diatomite followed by obtaining canasite will make it possible to decrease the glass making temperature by 200 – 250°C [3].

Lake diatomites without enrichment can also be used to obtain ceramics. Heat-insulating facing materials with low

thermal conductivity (0.03 – 0.6 W/(m · K)) have been developed, under laboratory conditions, on the basis of the D-00-50 diatomite and Cambrian clay from the Chkalov deposit [4].

In summary, the lake diatomites of Karelia are a promising raw material for manufacturing heat-insulating facing materials, water filters, and other articles. On account of the presence of active (hydrated) amorphous silicates lake diatomites from which impurities have been removed are of interest for the production of sheet glass, class articles, and glazes and enamels as well as silicate glasses with low expansion coefficient and high strength.

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